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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY  
OF THE CASE SCHOOL OF APPLIED SCIENCE.

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*INVESTIGATIONS ON AMERICAN PETROLEUM.*

BY CHARLES F. MABERY.

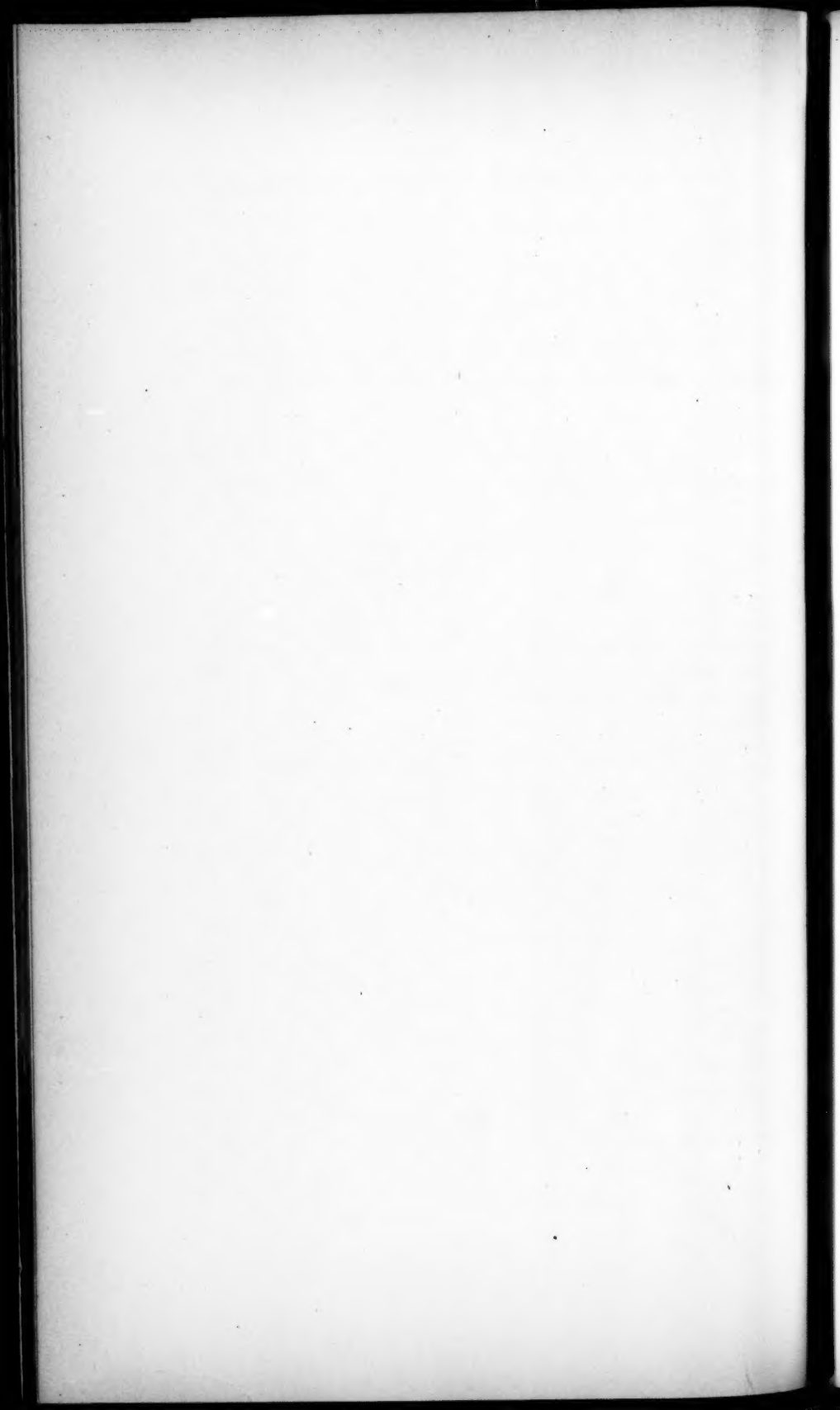
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XXVIII. — *REFRACTIVE POWER OF THE HYDROCAR-  
BONS AND CHLORINE DERIVATIVES DESCRIBED  
IN THE PRECEDING PAPER.*

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## XXVIII.— REFRACTIVE POWER OF THE HYDROCARBONS AND CHLORINE DERIVATIVES DESCRIBED IN THE PRECEDING PAPER.

BY CHARLES F. MABERY AND EDWARD J. HUDSON.

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WITHIN recent years the refractive power of the hydrocarbons and their derivatives has received considerable attention by Brühl, Thomsen, and others, and attempts have been made to draw conclusions based on the relation between the index of refraction and density, to define structural relations. The experimental data have been obtained for the most part from bodies with a limited number of carbon atoms, in which the differences in refractive power are large. Independent of determinations bearing on theoretical considerations, the refractive power of oils and solutions has been accepted on practical grounds as a valuable property for recognition and for determining degrees of purity.

While it was not to be expected that the determination of refractive power in hydrocarbons with such a large number of carbon atoms as those contained in the higher portions of petroleum would be serviceable in ascertaining the structure of individual hydrocarbons, the wide differences in specific gravity between unpurified and purified distillates led us to believe that similar differences should be observed in refractive power. When subjected to experimental proof, these differences were easily verified.

The determinations of the angle of refraction were made in the latest form of Pulfrich refractometer, made by Carl Zeiss, Jena, and the calculations of the index of refraction by the formula  $1 = \sqrt{N^2 - \sin^2 I}$ , in which 1 represents the index of refraction,  $N$  the angle of the prism, and  $I$  the observed angle. The observations in this refractometer are rapidly made, and the calculations are much simplified by the use of a table arranged by

Pulfrich\* so that from the observed angle the index may read directly from the table.

In the following table giving the refractive power (the excess of the index of refraction over unity), after the numbers representing the refractive power of the distillates purified by a mixture of nitric and sulphuric acids, and with fuming sulphuric acid, the differences between the refractive power before purification and afterwards are given.

	PENNSYLVANIA.		OHIO.		CANADA.
		163°.			
	Ref. Power, Dif.		Ref. Power, Dif.		Ref. Power, Dif.
Unpurified distillate	.4241		.4248		.4276
After treatment with					
HNO <sub>3</sub> and H <sub>2</sub> SO <sub>4</sub>	.4083 .0158		.4123 .0125		.4133 .0143
After treatment with					
H <sub>2</sub> S <sub>2</sub> O <sub>7</sub>	.4146 .0095		.4113 .0135		.4137 .0139
		173°.5			
Unpurified distillate	.4163		.4239		.4245
After treatment with					
HNO <sub>3</sub> and H <sub>2</sub> SO <sub>4</sub>	.4118 .0045		.4134 .0105		.4149 .0096
After treatment with					
H <sub>2</sub> S <sub>2</sub> O <sub>7</sub>	.4093 .0070		.4118 .0121		.4138 .0107
		196°.			
Unpurified distillate	.4214		.4251		.4309
After treatment with					
HNO <sub>3</sub> and H <sub>2</sub> SO <sub>4</sub>	.4158 .0056		.4214 .0037		.4219 .0090
After treatment with					
H <sub>2</sub> S <sub>2</sub> O <sub>7</sub>	.4163 .0051		.4209 .0042		.4231 .0078
		216°.			
Unpurified distillate	.4249		.4280		.4289
After treatment with					
HNO <sub>3</sub> and H <sub>2</sub> SO <sub>4</sub>	.4209 .0040		.4244 .0036		.4219 .0070
After treatment with					
H <sub>2</sub> S <sub>2</sub> O <sub>7</sub>	.4209 .0040		.4241 .0039		.4212 .0077

Inspection of the columns in this table headed Refractive Power shows a gradual increase with the rise in boiling points, less regular in the un-

\* Zeit. für Instrumentenkunde, 1888, p. 47.

purified distillates, but more uniform after purification. A comparison of refractive power in the same distillates from all the oils reveals higher values in the Ohio and Canadian distillates than in those from Pennsylvania oil, analogous to the differences in specific gravity referred to in the preceding paper. In the unpurified distillate  $163^{\circ}$  from all sources, the influence of the large proportions of mesitylene is apparent.

In determining the refractive power of the monochlor and dichlor derivatives of the hydrocarbons between  $160^{\circ}$  and  $216^{\circ}$ , portions of the product were used whose composition was determined by analysis, as shown in the preceding paper. On account of the limited quantities purification was not carried as far as would have been desirable, although the proportion of other bodies was probably not sufficient to affect seriously the results. The differences in refractive power between the hydrocarbons and the monochlor derivatives, as well as those between the monochlor and dichlor derivatives are sufficient to demonstrate the influence of the chlorine atoms.

## Monochlor derivatives: —

Distillate		PA.	OHIO.	CAN.
125-130 ( $C_{10}H_{21}Cl$ )	from $164^{\circ}$	.4424		
" "	" "		.4470	
130-140 ( $C_{10}H_{21}Cl$ )	" $174^{\circ}$	.4445		
" "	" "		.4437	
145-150 ( $C_{11}H_{23}Cl$ )	" $196^{\circ}$	.4433		
" "	" "		.4457	
" "	" "			.4461
140-145 ( $C_{12}H_{25}Cl$ )	" $216^{\circ}$	.4456		
" "	" "			.4521

## Dichlor derivatives: —

Distillate.				
160-170 ( $C_{10}H_{20}Cl_2$ )	from $164^{\circ}$	.4639		
" "	" "		.4770	
170-180 ( $C_{10}H_{20}Cl_2$ )	" $174^{\circ}$	.4604		
" "	" "		.4640	
" "	" "			.4676
190-200 ( $C_{12}H_{24}Cl_2$ )	" $216^{\circ}$	.4650		
" "	" "			.4747

It seems peculiar that the hydrocarbon 216° Canadian petroleum which gives analytical values corresponding to the formula  $C_{12}H_{24}$  should have the same boiling point as the corresponding constituent of Pennsylvania and Ohio oils, and that it should give a chlorine derivative with substantially the same boiling point. Probably a better understanding of this hydrocarbon will be gained in the study of the higher constituents, which is now in progress.

